

**Remarks**

Responsive to the March 3, 2010 final Office Action, and pursuant to a teleconference between Examiner Dollinger and Ms. Cottrell on May 6, 2010, Applicants submit herewith the verified translation of priority document DE 103 34 286.9 to supplement the prior response filed May 3, 2010. Applicants have cancelled claim 11 without prejudice to the subject matter found therein.

***Claim Rejections – 35 USC § 102***

Applicants hereby incorporate by reference the remarks made in the prior response of May 3, 2010. In light of these remarks, the cancellation of claim 11, and the attached verified translation of priority document DE 103 34 286.9 (Appendix A), Applicants respectfully request that the examiner withdraw the rejections of claims 1-6, 8-10, 18-20, 23, 24, and 28.



***Conclusion***

In light of the remarks and amendments to the claims presented herein, Applicants submit that the present application is in condition for allowance, and such action is respectfully requested. If, however, any issues remain unresolved, the Examiner is invited to telephone Applicants' counsel at the number provided below.

Respectfully submitted,

/Clara R. Cottrell/

Clara R. Cottrell  
Registration No. 63,861

SMITH MOORE LEATHERWOOD LLP  
P.O. Box 21927  
Greensboro, NC 27420  
(336) 378-5597  
clara.cottrell@smithmoorelaw.com

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# APPENDIX A

Verification of Translation and  
Translation of DE 103 34 286.9



# VERIFICATION OF TRANSLATION

I, Pall Franke - patent attorney  
of Evonik Stockhausen GmbH

declare as follows:

1. That I am well acquainted with both the English and German languages, and
2. that the attached document is a true and correct English translation controlled by me to the best of my knowledge and belief of:

German priority application DE 103 34 286.9

03.05.2010  
Date

P. Franke  
Signature



**Powdery water-absorbing polymers with fine particles bound by means of thermoplastic adhesives**

5

The present invention relates to powdery water-absorbing polymers, preferably superabsorbers, a process for producing powdery water-absorbing polymers, the powdery water-absorbing polymers obtainable by this process, a transport process, a composite, chemical products and the use of a thermoplastic adhesive.

Superabsorbers are water-insoluble, crosslinked polymers, which are able to absorb and to retain under pressure large quantities of water, aqueous liquids, in particular body liquids, preferably urine or blood, by swelling and formation of hydrogels. Superabsorbers absorb preferably at least 100 times their own weight in water. Further details concerning superabsorbers are disclosed in "Modern Superabsorbent Polymer Technology", F. L. Buchholz, A. T. Graham, Wiley, VCH, 1998. Because of these characteristic properties, these water-absorbing polymers are principally incorporated into sanitary articles, such as for example baby diapers, incontinence products or sanitary napkins.

Currently commercially available superabsorbers are substantially crosslinked polyacrylic acids or crosslinked starch-acrylic acid graft polymers, in which the carboxyl groups are partially neutralized with sodium hydroxide or potassium hydroxide. These are attainable by radically polymerising monomeric acrylic acid or respectively salts thereof in the presence of suitable crosslinking means. In this process, different polymerisation processes can be used, such as for example solution polymerisation, emulsion polymerisation or suspension polymerisation. Finally, water-absorbing polymers are obtained by these different processes in particulate form with a particle diameter within a range from 150 to 850  $\mu\text{m}$ , which are then incorporated into the sanitary article.



In order to improve the absorption and swelling capacity of these water-absorbing polymer particles, numerous processes have been described in which the surface of the polymer particles is modified. It is, for example, known from DE-A-40 20  
5 780 to convert the water-absorbing polymer particles with alkaline carbonates, which can react with the carboxyl groups of the polymer particles. The surface secondary crosslinking effected in this way leads to an increase of the absorption of the polymer under the action of a pressure.

10 Besides the conversion of the polymer particles with reactive compounds, in the prior art numerous processes are also described with which the properties of the water-absorbing polymer particles is achieved by means of a coating with inorganic or organic fine particles.

15 Thus in DE-A-35 03 458 it is described that the absorption capacity, the rate of absorption and the gel stability of superabsorber particles can be improved by the application of inert inorganic powder materials, such as for example silicon dioxide, in the presence of secondary crosslinking agents. To reduce the hygroscopy and thereby to reduce the caking of the polymer particles, EP-A-0 388 120 pro-  
20 poses the coating of the polymer particles with a porous powder of highly pure silicon dioxide, whereby the powder has an average particle size of 0.1 to 30  $\mu\text{m}$  and a specific surface of 500  $\text{m}^2/\text{g}$ .

DE-A-199 39 662 teaches that water-absorbing polymer structures are coated with  
25 particulate cyclodextrins and zeolites, in order to bind in this way compounds from body liquids which are characterized by an unpleasant odour.

A common problem in all these processes for subsequent modification is that they lead to a release of fine particles in the form of dust, whereby these fine particles  
30 arise through mechanical stress, such as for example by pneumatic conveying and thereupon-contingent abrasion of the water-absorbing polymer particles, or result



from a lacking adhesion to the surface of the absorbent fine particles of the inorganic or organic fine particles which are applied for the subsequent modification of the polymer particles.

- 5 The release of dust, in particular of dust with a particle size of less than 10  $\mu\text{m}$  is undesirable for reasons of inhalation toxicity; fine particles with a particle size of less than 100  $\mu\text{m}$  cause the visible dust with all its after-effects and lead to handling problems in production and processing distribution. Above all, the flowability of superabsorbers modified at the surface with inorganic or organic particles is  
10 negatively influenced by the lacking adhesion of these particles at the surface of the superabsorber particles.

The object underlying the present invention was thus, to overcome the disadvantages arising from the state of the art.

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In particular, the object underlying the present invention consisted in providing a process with which it is possible to produce superabsorber particles modified with inorganic or organic particles, said superabsorber particles having a sufficient adhesion of the organic or inorganic particles to the surface of the superabsorber  
20 particle.

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Further, the object of the present invention consisted in providing water absorbing particles which have excellent absorption properties, for example with respect to the absorption capacity, the permeability or the speed of absorption, and which  
25 have a satisfactory flow behaviour in transport in conveyor installations for producing hygiene articles and do not tend to form dust.

30

In addition, an object according to the invention consisted in providing water absorbing polymer particles which have excellent absorption properties, for example  
30 with respect to the absorption capacity, the permeability or the speed of absorption, and in addition are characterized by a good mechanical stability.



Additionally, the water absorbing polymer particles should, in their incorporation into a composite comprising a matrix of a fibrous material, enable a sufficient fixing within the composite by means of adhesion of the water absorbing polymer particles to the matrix fibres.

It was also an object of the present invention to provide a composite comprising water absorbing polymer particles, said composite having an at least comparable water absorption in comparison with the absorbent particles known from the state of the art by means of the excellent absorption properties of the water absorbing polymer particles or in which composite a satisfactory fixing of the water absorbing polymer particles within the composite is achieved, whereby the water absorbing polymer particles incorporated in the composite have an improved stability and/or a reduced tendency to dust.

One of the objects underlying the present invention consisted further in providing chemical products comprising the water absorbing polymer particles, which products have excellent absorption properties and are characterized by as low as possible a release of dust, for example during mechanical stress.

In addition, an object of the present invention consisted in providing a water absorbing polymer particle which is damaged to as small an extent as possible, and forms as little dust as possible, by the mechanical demands occurring during transport processes in the production of these polymer particles or during the further processing in dosing systems in Airlaid or diaper machines. The above objects are solved by powdery water absorbing polymers, by a process for producing powdery water absorbing polymers by powdery water absorbing polymers obtainable by this process, by a transport process, by a composite, by chemical products as well as by the use of a thermoplastic adhesive according to the respective category-forming claims. Advantageous embodiments of the powdery water absorbing polymers according to the invention or of the process according to the inven-



tion for producing these powdery water absorbing polymers are the subject matter of the dependent claims, which can respectively be individually applied or combined with each other in any way.

5 The powdery water absorbing polymers according to the invention comprise as components:

- 0.01 to 20 wt. %, preferably 0.05 to 15 wt. % and even more preferably 0.1 to 10 wt. % of a fine particle with a particle size determined by sieve analysis of less than 200  $\mu\text{m}$ , preferably from less than 100  $\mu\text{m}$  and particularly preferably less than 50  $\mu\text{m}$ ;
  - 0.001 to 10 wt. %, preferably 0.01 to 5 wt. % and particularly preferably 0.1 to 1 wt. % of a thermoplastic adhesive,
  - 60 to 99.998 wt. %, preferably 70 to 99 wt. % and particularly preferably 80 to 95 wt. % of a water absorbing polymer particle with a particle size determined by sieve analysis of at least 200  $\mu\text{m}$ , preferably of at least 250  $\mu\text{m}$  and particularly preferably of at least 300  $\mu\text{m}$ , whereby the sum of the above components amounts to 100 wt. %, wherein
- 20 the fine particles are bound to the surface of the water absorbing polymer particle by means of the thermoplastic adhesive and the powdery water absorbing polymers have either
- a flow value (FFC value) determined according to the test method described herein within the range from 1 to 13, preferably within the range from 3 to 9 and particularly preferably within the range from 4 to 8 and even more preferably within the range from 5 to 7, or
- 25 a dust portion determined according to the test method described herein of at most 6, preferably at most 4, particularly preferably at most 2. Preferably, the powdery water absorbing polymer particles have both flow value
- 30 (FFC value) and dust portion in the above-mentioned ranges.



According to an embodiment of the present invention, these fine particles are so-called superabsorber fine particles which arise during transport or sieving steps during the production and confectioning of superabsorbers.

- 5 In a further embodiment of the present invention, it is preferred that the fine particles are not superabsorbers and in particular are not based on water-absorbing, crosslinked, partially neutralized polyacrylic acids or salts thereof. Thus, for example, cyclodextrins are used as fine particles in the confectioning for odour management in hygiene articles, as described in EP 0 691 856 B1.

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The fine particles which are preferably not based on water-absorbing, crosslinked, partially neutralized polyacrylic acids or salts thereof are preferably organic, different to the water absorbing polymers, or inorganic fine particles.

- 15 As organic material, any particulate organic material known to the skilled person can be comprised in the powdery water absorbing polymers according to the invention, which is commonly used for modifying the properties of water absorbing polymers. Cyclodextrins or derivatives thereof as well as polysaccharides belong to the preferred organic fine particles. In addition, cellulose and cellulose derivatives such as CMC, cellulose ether are preferred.
- 20

- As cyclodextrins or cyclodextrin derivatives, those compounds are preferred which are disclosed in DE-A-198 25 486 on page 3, line 51 to page 3, line 61. The above-cited section of this published patent application is hereby introduced as reference and forms part of the disclosure of the present invention. Particularly preferred cyclodextrins are non-derivatised  $\alpha$ ,  $\beta$ ,  $\gamma$  or  $\delta$ -cyclodextrins. In the use of organic fine particles it is particularly preferred that these fine particles are comprised in the powdery water absorbing polymers in a quantity in a range from 0.1 to 1 wt. %, more preferably in a quantity within a range from 0.25 to 0.75 wt. % and even more preferably within a range from 0.4 to 0.6 wt. %. The proportions of
- 25
- 30



amounts given in the examples according to the invention have shown themselves to be particularly advantageous.

5 As inorganic material, any particulate inorganic material known to the skilled person can be comprised in the powdery water absorbing polymers according to the invention which is commonly used for modifying the properties of water absorbing polymers. Silicates, in particular scaffolding silicates such as zeolites or silicates which have been obtained by drying aqueous silicic acid solutions or silica  
10 sols belong to the preferred inorganic fine particles, for example the commercially obtainable products such as precipitation silicic acids and pyrogenic silicic acids, for example aerosols with a particle size within the range of 5 to 50 nm, preferably within the range of 8 to 20 nm such as "Aerosil 200" of Degussa AG, aluminates, titanium dioxides, zinc oxides, clay materials and further minerals common to the skilled person as well as carbon-containing inorganic materials.

15 Preferred silicates are all natural or synthetic silicates which are disclosed as silicates in "Holleman and Wiberg", Lehrbuch der Anorganischen Chemie, Walter de Gruyter Verlag, 91.-100. Edition, 1985" on pages 750 to 783. The above-mentioned section of this textbook is hereby introduced as reference and forms  
20 part of the disclosure of the present invention.

Particularly preferred silicates are the zeolites. As zeolites, all synthetic or natural zeolites known to the skilled person can be used. Preferred natural zeolites are zeolites from the natrolite groups, the harmotone groups, the modenite groups, the  
25 chabasite groups, the faujasite groups (sodalite groups,) or the analcite groups. Examples of natural zeolites are Analcime, Leucite, Pollucite, Wairakite, Bellbergite, Bikitaite, Boggsite, Brewsterite, Chabazite, Willhendersonite, Cowlesite, Dachiardite, Edingtonite, Epistilbite, Erionite, Faujasite, Ferrierite, Amicite, Garronite, Gismondine, Gobbinsite, Gmelinite, Gonnardite, Goosecreekite, Harmotome, Phillipsite, Wellsite, Clinoptilolite, Heulandite, Laumontite, Levyne,  
30 Mazzite, Merlinoite, Montesommaite, Mordenite, Mesolite, Natrolite, Scolecite,



Offretite, Paranatrolite, Paulingite, Perlialite, Barrerite, Stilbite, Stellerite, Thomsonite, Tschernichite oder Yugawaralite. Preferred synthetic zeolites are zeolite A, zeolite X, zeolite Y, zeolite P, or the product ABSCENTS.

5 As zeolites, zeolites of the so called “medium” (“mittlere”) type can be used, in which the  $\text{SiO}_2/\text{AlO}_2$  ratio is smaller than 10, particularly preferably the  $\text{SiO}_2/\text{AlO}_2$  ratio of these zeolites lies in a range of 2 to 10. Besides these “medium” zeolites, zeolites of the “high” (“hohe”) type can furthermore be used, to which belong for example the known “molecular sieve” zeolites of the type ZSM  
10 as well as beta-zeolites. These “high” zeolites are preferably characterized by a  $\text{SiO}_2/\text{AlO}_2$  ratio of at least 35, particularly preferably by a  $\text{SiO}_2/\text{AlO}_2$  ratio in a range of 200 to 500.

As aluminates, spinels occurring in nature, in particular common spinels, zinc  
15 spinel, iron spinel or chromium spinel are used.

Preferred titanium dioxides is pure titanium dioxide in the crystal forms rutile, anatase and brookite, as well as iron-containing titanium dioxides such as for example ilmenite, calcium-containing titanium dioxides such as titanite or  
20 perovskite.

Preferred clay materials are those which are disclosed as clay materials in “Holleman and Wiberg, Lehrbuch der Anorganischen Chemie, Walter De Gruyter Verlag, 91. to 100. Edition, 1985” on pages 783 to 785. The above-cited section of  
25 this textbook is hereby introduced as reference and forms part of the disclosure of the present invention. Particularly preferred clay materials are kaolinite, illite, halloysite, montmorillonite as well as talc.

Furthermore, the metal salts of mono, oligo- and polyphosphoric acids are preferred  
30 as inorganic fine particles according to the invention. Among these, in particular the hydrates are preferred, whereby the mono- to decahydrates and tri-



hydrates are particularly preferred. As metals, in particular alkali and alkaline earth metals are considered, whereby alkaline earth metals are preferred. Among these, Mg and Ca are preferred and Mg is particularly preferred. In the context of phosphates, phosphoric acids and metal compounds thereof, reference is made to  
5 “Holleman and Wiberg, Lehrbuch der Anorganischen Chemie, Walter De Gruyter Verlag, 91. to 100. Edition, 1985” on pages 651 to 669. The above-mentioned section of this textbook is hereby introduced as reference and forms part of the disclosure of the present invention.

10 Preferred carbon-containing, but non-organic materials, are those pure carbons which are mentioned as graphites in “Holleman and Wiberg, Lehrbuch der Anorganischen Chemie, Walter De Gruyter Verlag, 91. to 100. Edition, 1985” on pages 705 to 708. The above-mentioned section of this textbook is hereby introduced as reference and forms part of the disclosure of the present invention. Particularly  
15 preferred graphites are artificial graphites such as for example coke, pyrolytic graphite, active carbon or soot.

The fine particles comprised in the powdery water absorbing polymers according to the invention can be present in the form of fibres, foams or particles, whereby  
20 fibres and particles are preferred and particles particularly preferred. If organic polysaccharides, such as for example cellulose fine particles, are used as fine particles, it is then preferred that the fine particles are used in the form of fibres. These fibres preferably have a linear density within the range of 0.5 to 6 and particularly preferably of 0.7 to 4 detex. Further details of suitable fibres are dis-  
25 closed in EP-A-0 273 141.

In the use of organic or inorganic fine particles or of mixtures thereof described in the following, it is particularly preferred that these fine particles are comprised in the powdery water absorbing polymers in a quantity within a range of 0.1 to 1 wt.  
30 %, more preferably in a quantity within a range from 0.25 to 0.75 wt. % and even more preferably within a range of 0.4 to 0.6 wt. %. The proportions given in the



examples according to the invention have shown themselves as particularly advantageous, in particular for the above-detailed organic and inorganic individual compounds.

- 5 In a preferred embodiment of the powdery water absorbing polymers according to the invention, these comprise a component a mixture of an organic and an inorganic fine particle.

10 In a preferred embodiment of the powdery water absorbing polymer according to the invention, the fine particles which is preferably not based on water absorbing crosslinked poly(meth)acrylates comprises, to at least 80 wt. %, preferably to at least 90 wt. % and even more preferably to at least 95 wt. %, respectively based on the weight of the fine particle which is preferably not based on water absorbing crosslinked poly(meth)acrylates, an inorganic fine particle.

15 In another preferred embodiment of the powdery water absorbing polymer according to the invention, the fine particle which is preferably not based on water absorbing crosslinked poly(meth)acrylates comprises, to at least 80 wt. %, preferably to at least 90 wt. % and even more preferably to at least 95 wt. %, respectively  
20 based on the weight of the fine particle which is preferably not based on water absorbing crosslinked poly(meth)acrylates, an organic fine particle.

It is furthermore preferred according to the invention that the fine particles which are preferably not based on water absorbing, crosslinked, partially neutralized  
25 polyacrylic acids or salts thereof have a specific surface determined according to the BET method within a range of 30 to 850 m<sup>2</sup>/g, preferably within a range of 40 to 500 m<sup>2</sup>/g, particularly preferably within a range of 100 to 300 m<sup>2</sup>/g and even more preferably within a range from 150 to 250 m<sup>2</sup>/g. In general, and in the case that the fine particles are sipernates and aerosols, the surface lies within a range of  
30 30 to 850 m<sup>2</sup>/g, preferably within a range from 40 to 500 m<sup>2</sup>/g, particularly preferably within a range from 100 to 300 m<sup>2</sup>/g and is determined with nitrogen in an



area meter according to ISO 5794, Annex D. In a preferred embodiment of the powdery water absorbing polymer according to the invention, at least 90 wt. %, preferably at least 95 wt. % and even more preferably at least 99 wt. % of the fine particles which are preferably not based on water absorbing crosslinked polyacrylates a particle size of less than 200  $\mu\text{m}$ , particularly preferably of less than 100  $\mu\text{m}$  and even more preferably of less than 1  $\mu\text{m}$  and even more preferably of less than 500 nm and yet further preferably of less than 100 nm. The sipernates have a particle size within the range of 10 to 180  $\mu\text{m}$ , preferably within the range of 20 to 150  $\mu\text{m}$  and particularly preferably within the range of 30 to 110  $\mu\text{m}$ . The particle size can be determined according to ASTM C 690-1992 with a Multisizer. In another embodiment of the present invention the sipernates have a mean particle size within the range of 1 to 40  $\mu\text{m}$ , preferably within the range of 2 to 30  $\mu\text{m}$  and particularly preferably within the range of 3 to 20  $\mu\text{m}$  as determined according to ASTM C 690-1992.

By a "thermoplastic adhesive" is preferably understood according to the invention a material which has no adhesive properties below a given temperature. Above a given temperature, preferably above the melting point of the material, the material shows sticky properties or adhesive properties, whereby these properties also remain in the solidified state after binding two substrates in the molten state. Preferably, the respective sticky or adhesive properties appear at least 10°C, preferably at least 20°C and particularly preferably within a range of 21 to 100°C above the melting point, determined by differential scanning calometry (DSC), of the material or material mixture used as thermoplastic adhesive. It is also possible in the present invention to use thermoplastic adhesives which comprise two ore more different compounds. The two ore more compounds can differ from each other in the chemical composition or in their molecular weight or in both.

The thermoplastic adhesives are preferably used as particles. Of these particles, preferably at least 50 wt. % and particularly preferably at least 70 wt. % of the particles have a particle size within the range of 10 to 500  $\mu\text{m}$ , preferably 25 to



250  $\mu\text{m}$  and even more preferably 40 to 120  $\mu\text{m}$ . The particle sizes can be determined by sieve analysis up to a size of 20  $\mu\text{m}$ . For particle sizes of less than 20  $\mu\text{m}$ , light scattering can be used to determine the particle size.

5 As thermoplastic adhesives, polymeric materials with a molecular weight of more than about 1000 g/mol are generally suitable, which have a corresponding melting temperature and at a corresponding application temperature do not decompose or show any alteration of the molecular composition which would otherwise be disadvantageous for the adhesive effect.

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The number average molecular weight ( $M_n$ ) determined by gel permeation chromatography (GPC) of the polymers which can be used as thermoplastic adhesives preferably lies between about 10,000 and about 1,000,000, particularly preferably between about 20,000 and about 300,000 and even more preferably between about  
15 50,000 and about 150,000 g/mol.

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The molecular weight distribution of the cited polymers, as can likewise be determined by gel permeation chromatography (GPC) can be monomodal. Optionally, a polymer usable as thermoplastic adhesive can also have a bi- or higher-modal distribution.

25

The compounds which can be used as thermoplastic adhesives in the present invention comprise to a portion of at least 60 wt. %, preferably to a portion of 80 wt. % and even more preferably to a portion of 100 wt. %, respectively based on the total weight of the thermoplastic adhesive, a melting temperature according to  
ISO 11357 of at least 50°C, preferably of at least 60°C and even more preferably of at least 70°C, whereby preferably a melting temperature according to ISO 11357, of 300°C, particularly preferably of 250°C and even more preferably of 200°C is not exceeded.

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The thermoplastic adhesives which can be used in the present invention should be not only solid but also have a non-sticky surface, at temperatures of up to about 30°C, preferably however at temperatures lying there above, for example at up to 40°C or up to 50°C.

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Already a little above the melting temperature, the thermoplastic adhesive should have relatively low viscosity. Preferably, its melt viscosity according to Brookfield (ASTM E 28) with a number 27 spindle at a temperature of 160°C should be smaller than 2,000 Pas, preferably smaller than 1,200 Pas and particularly preferably smaller than 600 Pas.

10

As thermoplastic adhesive, in the present invention a material is preferably used which comprises to at least 10 wt. %, preferably to at least 50 wt. % and particularly preferably to at least 90 wt. %, respectively based on the total weight of the thermoplastic adhesive, a polymer selected from polyurethanes, polyesters, polyamides, polyolefins, polyvinyl esters, polyethers, polystyrenes, polyimides, in particular polyether imides, sulfur polymers, in particular polysulfones, polyacetals, in particular polyoxymethylene, fluoride plastics, in particular polyvinylidene fluoride, styrene-olefin copolymers, polyacrylates or ethylene-vinyl acetate copolymers or mixtures of two or more of the cited polymers, whereby among these polymers polycondensates and among these polyesters are particularly preferred.

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As polyurethanes, in the present invention are to be understood all polymers which have at least two urethane groups in the polymer backbone.

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As polyurethane, in the present invention all thermoplastic polyurethanes known to the skilled person in the area of polyurethane chemistry are suitable, in particular such polyurethanes as are used commonly in the production of thermoplastic formed bodies, in particular of films, or for thermoplastic coating of surfaces. For example, polyester polyurethanes or polyether polyurethanes are suitable, as are obtainable by conversion of dicarboxylic acids with corresponding polyfunctional

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alcohols, in particular difunctional alcohols, for example difunctional polyethers such as polyethylene oxide, to polyether- or polyester polyols and then conversion of the corresponding polyether- or polyester polyols with di- or polyfunctional isocyanates. Particularly preferred thermoplastic polyurethanes are those polyure-  
5 thanes which are distributed by the company Kern GmbH, Großmeiseid, Germany, under the product code "TPU D", "TPU 93 A", "TPU 80 A" and "TPU GF 20". A further preferred thermoplastic polyurethane is the polyurethane with the product number "6005" distributed by the company Schaetti AG, Zurich, Switzerland under the product code "SchaettiFix®".

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As polyester, in the present invention should be understood all polymers which have at least two ester groups and no urethane groups in the polymer backbone. As polyester in the present invention, all thermoplastic polyesters known to the skilled person are suitable, in particular such polyesters as are commonly used in  
15 the production of thermoplastic formed bodies, in particular of films, or for thermoplastic coating of surfaces. For example, polyesters are suitable, as obtainable by conversion of dicarboxylic acids with corresponding polyfunctional alcohols, in particular difunctional alcohols, for example difunctional polyethers such as polyethylene oxide. Among these, polyesters are preferred, which are composed  
20 of terephthalic acid or a derivative thereof, isophthalic acid or a derivative thereof, adipinic acid or isophthalic acid or a derivative thereof, adipinic acid or a derivative thereof and at least one polyol, preferably butanediol or ethylene glycol or mixtures thereof. In an embodiment of the ester, it is preferred that in the ester the terephthalic acid or a derivative thereof, isophthalic acid or a derivative thereof or  
25 mixtures thereof are comprised in a quantity within the range of 30 to 80 wt. % and preferably in a quantity within the range of 40 to 65 wt. %. A further embodiment of the ester comprises adipinic acid or a derivative thereof in a quantity within the range of 3 to 20 wt. % and preferably in a quantity within the range from 5 to 15 wt. %. Furthermore, another embodiment of the ester comprises at  
30 least one polyol, preferably butanediol or ethylene glycol or mixture thereof, in a quantity within the range of 25 to 55 wt. % and preferably in a quantity within the



range of 30 to 40 wt. %. The above wt. % amounts are always based on the respective ester.

Particularly preferred thermoplastic polyesters are those polyesters which are distributed by the company Kern GmbH, Großmaischeid, Germany, under the product codes "PET", "PBT", "PBT V 0", "PC", "PC V 0", "PC FDA", "PC GF 10 V0" and "PC GF 30". Particularly preferred are furthermore those thermoplastic polyesters which are distributed by the company Schaetti AG, Zurich, Switzerland, under the product code "SchaettiFix" under the product numbers "373", "374", "376", "386", "386 F", and "399". Also preferred are the thermoplastic copolyesters which are distributed by the company Degussa AG, Düsseldorf, Germany, under the product codes "Dynacoll 7000", "Dynacoll 7380", "Dynacoll 7340", "Vestamelt 4280", "Vestamelt 4481", "Vestamelt 4580" and "Vestamelt 4680/4681".

As polyamides, in the present invention all plastic polyamides are suitable as obtainable by conversion of suitable di- or polycarboxylic acids with corresponding amines. In a preferred embodiment of the present invention, polyamides are used which were at least partially produced by using dimeric fatty acids as dicarboxylic acids. In a further preferred embodiment of the present invention, as melt adhesive, nylon types are used, for example, nylon-6,6, nylon-6,9 or nylon-6,12.

Particularly preferred thermoplastic polyamides are those polyamides which are distributed by the company Kern GmbH, Großmaischeid, Germany under the product codes "PA 6 E", "PA 6", "PA 6 flex", "PA 6 V 0", "PA 6 MoS2", "PA 6 M 30", "PA 6 M 30 V 0", "PA 6 G 210", "PA 6 G 210 H", "PA 6 G 212", "PA 6 G 216", "PA 6 G 210 Ö1", "PA 6 G 210 AX", "PA 6 G 210 MoS2", "PA 6 G 210 AX", "PA 66 E", "PA 66", "PA 66 H", "PA 66 PE", "PA 6/6T", "PA 12 E", "PA 12" and "PA 12 G". Particularly preferred are further those thermoplastic polyamides which are distributed by the company Schaetti AG, Zurich, Switzerland under the product code "SchaettiFix<sup>®</sup>" and the product numbers "5018", "5047",



“5045”, “5005”, “5000”, “5010”, and “5065”. Further preferred polyamides are thermoplastic polyamides which are distributed by the company Degussa AG, Düsseldorf, Germany under the product codes “Vestamelt 171”, “Vestamelt 250”, “Vestamelt 251”, “Vestamelt 253”, “Vestamelt 350”, “Vestamelt 351”, “Vestamelt 353”, “Vestamelt 430”, “Vestamelt 432”, “Vestamelt 450”, “Vestamelt 451”, “Vestamelt 470”, “Vestamelt 471”, “Vestamelt 640”, “Vestamelt 722”, “Vestamelt 730”, “Vestamelt 732”, “Vestamelt 733”, “Vestamelt 742”, “Vestamelt 750”, “Vestamelt 753”, “Vestamelt 755”, “Vestamelt 840”, “Vestamelt X 1301”, “Vestamelt 3041”, “Vestamelt 3261”, “Vestamelt X 4685”, “Vestamelt X 7079” and “Vestamelt X 1010”.

The suitable polyolefins in the present invention are for example obtainable by radical or coordinative polymerization of alpha-olefins, in particular of ethylene or propylene. In the present invention, both homopolymers and copolymers are suitable for use as thermoplastic adhesive. If copolymers should be used as thermoplastic adhesive, it is then preferred in the present invention if such thermoplastic adhesives comprise at least a portion of atactic copolymers, preferably however substantially comprise atactic copolymers. For producing corresponding compounds, suitable processes are known to the skilled person.

Particularly preferred thermoplastic polyolefins are those polyethylenes and polypropylenes which are distributed by the company Kern GmbH, Großmaiseid, Germany, under the product codes “PE UHMW”, “PE HMW”, “PE HMW ELS”, “PE HD”, “PE LD”, “PP-H”, “PP-C”, “PP-C HI”, “PP V2”, “PP M20” and “PP M40”. Particularly preferred are further those thermoplastic ethylenes which are distributed by the company Schaetti AG, Zurich, Switzerland under the product code “SchaettiFix<sup>®</sup>” and the product numbers “1800”, “1820”, “1822”, “1825”, “120” and “140”.

As polyvinyl ester, in the present invention, in particular polymers and copolymers of vinyl acetates are suitable. In a preferred embodiment, copolymers of vi-



nyl acetate with alpha-olefins, in particular with ethylene, are used. Preferably, the copolymers have a vinyl acetate content of about 15 to about 40 %, in particular about 18 to about 25 %. The melt index of polymers of this type preferably lies at about 150 to about 500, measured according to ASTM D 1238.

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Particularly preferred thermoplastic polyvinyl esters are those polyvinylesters which are distributed by the company Schaetti AG, Zurich, Switzerland under the product code "SchaettiFix<sup>®</sup>" and the product numbers "2047", "2048", "1303", and "2050".

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In the present invention, suitable polyethers are, for example, polyethylene oxide, polypropylene oxide, polybutylene oxide or polytetrahydrofuran, in particular with a molecular weight of greater than about 5,000.

15 As polystyrenes, polymers of styrene or  $\alpha$ -methylstyrene are, for example, suitable.

Likewise suitable as polymers for the thermoplastic adhesives are styrene-olefin block copolymers, as obtainable by copolymerisation of styrene with mono- or  
20 diolefins, in particular butadiene. Particularly suitable in this context are the polymers referred to as synthetic rubbers, as are obtainable from the copolymerization of styrene and butadiene or styrene and isoprene. Likewise suited in the present invention are synthetic rubbers of the cited type, which have been subjected to a partial or full hydration. In the present invention synthetic rubbers usable as thermoplastic adhesives in the present invention preferably have a number  
25 average molecular weight of about 70,000 to about 200,000, for example about 80,000 to about 150,000.

Particularly preferred thermoplastic polymers based on styrene are those styrene  
30 polymers which are distributed by the company Kern GmbH, Großmaiseid,



Germany under the product codes “PS”, “PS V2”, “SB”, “SB V0”, “SB ELS”, “ABS”, “ABS V0”, “ABS EMV”, “SAN”, “ASA” and “ASA HI”.

5 The terms “polyacrylate” or “polyacrylates”, as used in the present text, in the context of the thermoplastic adhesive, refer in the following both to polymers or copolymers of acrylic acid and/or its derivatives and to polymers or copolymers of methacrylic acid and/or its derivatives.

10 Polyacrylates can be produced, in that acrylic acid and/or methacrylic acid and/or derivatives of acrylic acid and/or methacrylic acid, for example esters thereof with mono- or polyfunctional alcohols, respectively alone or as a mixture of two or more thereof, are polymerised in known ways, for example radically or ionically.

15 In the present invention, as thermoplastic adhesive based on polyacrylates, homopolymers or copolymers which have, besides the acrylic acid esters (acrylates) additionally styrene, acrylonitrile, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, ethylene, propylene and/or butadiene, can be used.

20 As monomer, in the production of thermoplastic adhesives based on polyacrylates, are considered in particular methacrylate, ethyl acrylate, n-butylacrylate, isobutyl acrylate, tert-butylacrylate, hexylacrylate, 2-ethyl-hexylacrylate or laurylacrylate. Optionally, as further monomers, additionally acrylic acid, methacrylic acid, acrylamide or methacrylamide can be added in small quantities during the polymerisation.

25

Optionally, yet further acrylates and/or methacrylates with one or more functional groups can be present during the polymerisation. For example, these are maleic acid, itaconic acid, butanediol diacrylate, hexanediol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, trimethylpropane triacrylate, 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, hydroxypropyl acrylate, propylene glycol methacrylate, butanediol monoacrylate,

30



ethyl diglycol acrylate, as well as sulfonic acid group-carrying monomers, for example 2-acrylamido-2-methyl propane sulfonic acid. Particularly preferred are acrylic ester vinyl ester copolymers, acrylic ester styrene copolymers or acrylic ester methacrylic ester copolymers.

5

In a further preferred embodiment, in the powdery, water-absorbing polymers according to the invention, copolymers of acrylic acid and styrene are comprised as thermoplastic adhesive based on polyacrylates, whereby the monomer ratio in melt adhesives of this type amounts to about 70: 30 (styrene: acrylic acid).

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The thermoplastic adhesives comprised in the powdery water absorbing polymers according to the invention comprise at least one of the above compounds. It is, in the present invention, however, also possible that the thermoplastic adhesives used comprise two or more of the cited compounds.

15

In a further preferred embodiment of the invention, the thermoplastic adhesive comprises at least two polymers selected from the group consisting of vinyl acetate homo polymers, vinyl acetate copolymers, poly-alpha-olefins, polyacrylates, polymethacrylates, polyacrylic acid esters, polymethacrylic acid esters, polyethers, polyesters, polyamides or polyurethanes.

20

Besides one or more of the above-mentioned polymers, a thermoplastic adhesive, as comprised in the powdery water absorbing polymers according to the invention, can comprise yet further additives, which allow a modification of the adhesive properties. For example, the so called tackifier-resins are suitable for this purpose, which can be sub-divided into natural resins and synthetic resins (artificial resins). Suitable tackifier-resins are, for example, alkyd resins, epoxide resins, melamine resins, phenol resins, urethane resins, hydrocarbon resins as well as natural resins from colophony, wood turpentine, and tall oil. As synthetic hydrocarbon resins, for example ketone resins, coumarone-indene resins, isocyanate

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resins and terpene-phenol resins are suitable. In the present invention, synthetic resins are preferred.

5 Resins of this type can be comprised in the thermoplastic adhesives comprised in the powdery water absorbing polymers according to the invention in a quantity of up to about 50 wt. %, preferably up to 60 wt. % and particularly preferably up to 70 wt. %, respectively based on the thermoplastic adhesive, for example in a quantity of about 0.1 to about 35 wt. % or about 3 to about 20 wt. %.

10 Besides the already mentioned components, a thermoplastic adhesive, as is comprised in the powdery water absorbing polymers according to the invention, can additionally comprise at least one wax. By a "wax", in the present invention, is understood a water-insoluble compound or a mixture of two or more of such compounds with a melting point of 90 to about 165°C. Suitable waxes are, for  
15 example, paraffin waxes, polyethylene waxes, polypropylene waxes, montan waxes, Fischer-Tropsch waxes, microcrystalline waxes or carnauba waxes.

Waxes of this type can be present in a thermoplastic adhesive, as can be used in the present invention, in a quantity of up to 60 wt. %, preferably up to 70 wt. %  
20 and particularly preferably up to 80 wt. %, respectively based on the thermoplastic adhesive, for example in a quantity of about 5 to about 60 wt. %. If compounds are used in the present invention as thermoplastic adhesives, which are obtainable from the polymerisation of alpha-olefins, the portion of waxes in melt adhesives of this type preferably amounts to at least about 5 wt. % or at least about 10 wt.  
25 %.

It is further preferred in a design of the present invention, that the thermoplastic adhesive is applied to the powdery water absorbing polymer as a liquid phase. For this purpose, besides solutions of the thermoplastic adhesive, emulsions and dis-  
30 persions are suitable. As solvents for this liquid phase, all organic and inorganic solvents known to the skilled person are considered suitable. The liquid phases



comprise the thermoplastic adhesive in a quantity within the range of 0.001 to 50 wt. %, preferably within a range of 0.01 to 25 wt. % and particularly preferably within the range of 0.1 to 15 wt. %, respectively based on the solvent quantity. Particularly preferably, the liquid phase comprises as solvent to at least 60 wt. %, preferably to at least 80 wt. % water. It is further preferred that the liquid phase has at least one of the following described secondary crosslinkers, whereby in this context secondary crosslinker quantities within a range of 0.001 to 20 wt. % are preferred and within a range of 0.01 to 10 wt. % are particularly preferred.

Among the above disclosed thermoplastic adhesives, sulfonated thermoplastic adhesives are particularly suitable for use in liquid phases. Among these, sulfonated polyesters, sulfonated polyamides such as nylon are particularly preferred. A further group of thermoplastic adhesives suitable for liquid phases are polyethoxylated polyamides such as nylon, for example obtainable as Lurotex® from BASF AG in Ludwigshafen. Additionally suitable for use in liquid phases are styrene acrylic acid copolymers such as Joncryl® from SC Johnson, block copolymers comprising polyurethane and polyethylene oxide blocks, at least partially hydrolysed ethylene vinyl acetate copolymers and emulsions comprising polyacrylate and polyesters.

20

In a preferred embodiment of the powdery water-absorbing polymers according to the invention, the water-absorbing polymer particles comprised in the polymers are based on:

(α1) 0.1 to 99.999 wt.%, preferably 20 to 98.99 wt.% and particularly preferably 30 to 98.95 wt.% of polymerised, ethylenically unsaturated, acidic group-containing monomers or salts thereof, or polymerised, ethylenically unsaturated monomers containing a protonated or a quaternary nitrogen, or mixtures thereof, wherein mixtures comprising at least ethylenically unsaturated, acidic groups-containing monomers, preferably acrylic acid, are particularly preferred,

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- ( $\alpha$ 2) 0 to 70 wt.%, preferably 1 to 60 wt.% and particularly preferably 1 to 40 wt.% of polymerised, ethylenically unsaturated monomers which can be co-polymerised with ( $\alpha$ 1),
- 5 ( $\alpha$ 3) 0.001 to 10 wt.%, preferably 0.01 to 7 wt.% and particularly preferably 0.05 to 5 wt.% of one or more cross-linkers,
- ( $\alpha$ 4) 0 to 30 wt.%, preferably 1 to 20 wt.% and particularly preferably 5 to 10 wt.% of water soluble polymers, as well as
- ( $\alpha$ 5) 0 to 20 wt.%, preferably 0.01 to 7 wt.% and particularly preferably 0.05 to 5 wt.% of one or more auxiliaries, wherein the sum of the component
- 10 weights ( $\alpha$ 1) to ( $\alpha$ 5) amounts to 100 wt.%.

The monoethylenically unsaturated, acid group-containing monomers ( $\alpha$ 1) can be partially or fully, preferably partially neutralized. Preferably the monoethylenically unsaturated, acid group-containing monomers are neutralized to at least 25

15 mol%, particularly preferably to at least 50 mol% and even more preferably to 50 to 90 mol%. The neutralization of the monomers ( $\alpha$ 1) can occur before and also after the polymerisation. Further, the neutralization can occur with alkali metal hydroxides, alkaline earth metal hydroxides, ammonia as well as carbonates and bicarbonates. In addition, every further base is conceivable which forms a water-

20 soluble salt with the acid. A mixed neutralization with different bases is also conceivable. Neutralization with ammonia or with alkali metal hydroxides is preferred, particularly preferred with sodium hydroxide or with ammonia.

Furthermore, in a polymer the free acid groups can predominate, so that this

25 polymer has a pH value lying in the acid range. This acidic water-absorbing polymer may be at least partially neutralised by a polymer containing free basic groups, preferably amine groups, that is basic compared to the acidic polymer. These polymers are termed "mixed-bed ion-exchange absorbent polymers"



(MBIEA polymers) in the literature and are disclosed in, inter alia, WO 99/34843. The disclosure of WO 99/34843 is introduced here by way of reference and is thus part of the disclosure. As a rule MBIEA polymers represent a composition that contains on the one hand basic polymers that are able to exchange anions, and on the other hand contains a polymer that is acidic compared to the basic polymer and that is able to exchange cations. The basic polymer contains basic groups and is typically obtained by the polymerisation of monomers that carry basic groups or groups that can be converted into basic groups. These monomers are in particular those that contain primary, secondary or tertiary amines or the corresponding phosphines or at least two of the aforementioned functional groups. This group of monomers includes in particular ethyleneamine, allylamine, diallylamine, 4-aminobutene, alkyloxycycline, vinylformamide, 5-aminopentene, carbodiimide, formaladin, melamin and the like, as well as their secondary or tertiary amine derivatives.

Preferred monoethylenically unsaturated, acidic group-containing monomers ( $\alpha 1$ ) are acrylic acid, methacrylic acid, ethacrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -cyanoacrylic acid,  $\beta$ -methylacrylic acid (crotonic acid),  $\alpha$ -phenylacrylic acid,  $\beta$ -acryloxypropionic acid, sorbinic acid,  $\alpha$ -chlorosorbinic acid, 2'-methylisocrotonic acid, cinnamic acid, p-chlorocinnamic acid,  $\beta$ -stearic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene and maleic acid anhydride, wherein acrylic acid and methacrylic acid are particularly and acrylic acid even more particularly preferred.

Besides these carboxylate group-containing monomers, further preferred monoethylenically unsaturated acidic group-containing monomers ( $\alpha 1$ ) are ethylenically unsaturated sulfonic acid monomers or ethylenically unsaturated phosphonic acid monomers.



Preferred ethylenically unsaturated sulfonic acid monomers are allylsulfonic acid or aliphatic or aromatic vinylsulfonic acids or acrylic or methacrylic acids. Preferred aliphatic or aromatic vinylsulfonic acids are vinylsulfonic acid, 4-vinylbenzylsulfonic acid, vinyltoluenesulfonic acid and styrenesulfonic acid. Preferred acrylic or methacrylic acids are sulfoethyl(meth)acrylate, sulfopropyl(meth)acrylate and 2-hydroxy-3-methacryloxypropylsulfonic acid. As (meth)acrylamidoalkylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid is preferred.

10 Additionally preferred are ethylenically unsaturated phosphonic acid monomers, such as vinylphosphonic acid, allylphosphonic acid, vinylbenzylphosphonic acid, (meth)acrylamidoalkylphosphonic acids, acrylamidoalkyldiphosphonic acids, phosphonomethylated vinylamines and (meth)acrylphosphonic acid derivatives.

15 It is preferred according to the invention that the water-absorbing polymer comprises at least 50 wt.%, preferably at least 70 wt.% and more preferably at least 90 wt.% carboxylate group-containing monomers. It is particularly preferred according to the invention that the water-absorbing polymer comprises at least 50 wt.%, preferably at least 70 wt.% acrylic acid, which is neutralised preferably to at least 20 mol%, particularly preferably to at least 50 mol%.

Preferred ethylenically unsaturated monomers ( $\alpha 1$ ) containing a protonated nitrogen are preferably dialkylaminoalkyl(meth)acrylates in the protonated form, for example dimethylaminoethyl(meth)acrylate hydrochloride or dimethylaminoethyl(meth)acrylate hydrosulfate, as well as dialkylaminoalkyl(meth)acrylamides in the protonated form, for example dimethylaminoethyl(meth)acrylamide hydrochloride, dimethylaminopropyl(meth)acrylamide hydrochloride, dimethylaminopropyl(meth)acrylamide hydrosulfate or dimethylaminoethyl(meth)acrylamide hydrosulfate.



Preferred ethylenically unsaturated monomers ( $\alpha 1$ ) containing a quaternated nitrogen are dialkylammoniumalkyl(meth)acrylates in quaternated form, for example trimethylammoniummethyl(meth)acrylate-methosulfate or dimethylethylammoniummethyl(meth)acrylate-ethosulfate as well as (meth)acrylamidoalkyldialkylamine in quaternated form, for example (meth)acrylamidopropyltrimethylammonium chloride, trimethylammoniummethyl(meth)acrylate chloride or (meth)acrylamidopropyltrimethylammonium sulfate.

10

Preferred monoethylenically unsaturated monomers ( $\alpha 2$ ) which can be copolymerised with ( $\alpha 1$ ) are acrylamides and (meth)acrylamides.

Possible (meth)acrylamides besides acrylamide and methacrylamide are alkyl-substituted (meth)acrylamides or aminoalkyl-substituted derivatives of (meth)acrylamide such as N-methylol(meth)acrylamide, N,N-dimethylamino(meth)acrylamide, dimethyl(meth)acrylamide or diethyl(meth)acrylamide. Possible vinylamides are for example N-vinylamides, N-vinylformamides, N-vinylacetamides, N-vinyl-N-methylacetamides, N-vinyl-N-methylformamides, vinylpyrrolidone. Among these monomers acrylamide is particularly preferred.

Furthermore, as monoethylenically unsaturated monomers ( $\alpha 2$ ) which are copolymerisable with ( $\alpha 1$ ) are preferred monomers which are dispersible in water. As monomers which are dispersible in water are preferred acrylic acid esters and methacrylic acid esters, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate or butyl(meth)acrylate, as well as vinyl acetate, styrene and isobutylene.



Preferred cross-linkers ( $\alpha 3$ ) according to the invention are compounds which have at least two ethylenically unsaturated groups in one molecule (cross-linker class I), compounds which have at least two functional groups which can react with functional groups of the monomers ( $\alpha 1$ ) or ( $\alpha 2$ ) in a condensation reaction (= condensation cross-linkers), in an addition reaction or a ring-opening reaction (cross-linker class II), compounds which have at least one ethylenically unsaturated group and at least one functional group which can react with functional groups of the monomers ( $\alpha 1$ ) or ( $\alpha 2$ ) in a condensation reaction, an addition reaction or a ring-opening reaction (cross-linker class III), or polyvalent metal cations (cross-linker class IV). Thus with the compounds of cross-linker class I a cross-linking of the polymer is achieved by radical polymerisation of the ethylenically unsaturated groups of the cross-linker molecules with the monoethylenically unsaturated monomers ( $\alpha 1$ ) or ( $\alpha 2$ ), while with the compounds of cross-linker class II and the polyvalent metal cations of cross-linker class IV a cross-linking of the polymer is achieved respectively via condensation reaction of the functional groups (cross-linker class II) or via electrostatic interaction of the polyvalent metal cation (cross-linker class IV) with the functional groups of the monomer ( $\alpha 1$ ) or ( $\alpha 2$ ). With compounds of cross-linker class III a cross-linking of the polymers is achieved correspondingly by radical polymerisation of the ethylenically unsaturated groups or also by condensation reaction between the functional groups of the cross-linkers and the functional groups of the monomers ( $\alpha 1$ ) or ( $\alpha 2$ ).

Preferred compounds of cross-linker class I are poly(meth)acrylic acid esters, which have been obtained for example by conversion of a polyol, such as for example ethylene glycol, propylene glycol, trimethylolpropane, 1,6-hexanediol, glycerine, pentaerythritol, polyethyleneglycol or polypropyleneglycol, of an aminoalcohol, a polyalkylenepolyamine, such as for example diethylenetriamine or triethylenetetraamine, or of an alkoxidised polyol with acrylic acid or methacrylic acid. Further preferred compounds of cross-linker class I are polyvinyl com-



pounds, poly(meth)allyl compounds, (meth)acrylic acid esters of a monovinyl compound or (meth)acrylic acid esters of a mono(meth)allyl compound, preferably of the mono(meth)allyl compounds of a polyol or of an aminoalcohol. In this context DE 195 43 366 and DE 195 43 368 are referred to. The disclosures are  
5 included here by reference and are considered as part of the disclosure.

As examples of compounds of cross-linker class I are named alkenyldi(meth)acrylates, for example ethyleneglycoldi(meth)acrylate, 1,3-propyleneglycoldi(meth)acrylate, 1,4-butyleneglycoldi(meth)acrylate, 1,3-butylene-  
10 glycoldi(meth)acrylate, 1,6-hexanedioldi(meth)acrylate, 1,10-decanedioldi(meth)acrylate, 1,12-dodecanedioldi(meth)acrylate, 1,18-octadecanedioldi(meth)acrylate, cyclopentanedioldi(meth)acrylate, neopentylglycoldi(meth)acrylate, methylenedi(meth)acrylate or pentaerythritoldi(meth)acrylate, alkenyldi(meth)acrylamides, for example N-methyl-  
15 di(meth)acrylamide, N,N'-3-methylbutylidenebis(meth)acrylamide, N,N'-(1,2-dihydroxyethylene)bis(meth)acrylamide, N,N'-hexamethylenebis(meth)acrylamide or N,N'-methylenebis(meth)acrylamide, polyalkoxydi(meth)acrylates, for example diethyleneglycoldi(meth)acrylate, triethyleneglycoldi(meth)acrylate, tetraethyleneglycoldi(meth)acrylate, dipropylene-  
20 glycoldi(meth)acrylate, tripropyleneglycoldi(meth)acrylate or tetrapropylene-glycoldi(meth)acrylate, bisphenol-A-di(meth)acrylate, ethoxylated bisphenol-A-di(meth)acrylate, benzylidenedi(meth)acrylate, 1,3-di(meth)acryloyloxypropanol-2, hydroquinonedi(meth)acrylate, di(meth)acrylate esters of trimethylolpropane which is alkoxylated, preferably ethoxylated, preferably with 1 to 30 mol alkylene  
25 oxide per hydroxyl group, thioethyleneglycoldi(meth)acrylate, thiopropyleneglycoldi(meth)acrylate, thiopolyethyleneglycoldi(meth)acrylate, thiopolypropylene-glycoldi(meth)acrylate, divinyl ethers, for example 1,4-butanedioldivinyl ether, divinyl esters, for example divinyl adipate, alkanedienes, for example butadiene or 1,6-hexadiene, divinylbenzene, di(meth)allyl compounds, for example  
30 di(meth)allyl phthalate or di(meth)allyl succinate, homo- and co-polymers of di(meth)allyldimethylammonium chloride and homo- and co-polymers of di-



ethyl(meth)allylaminomethyl(meth)acrylateammonium chloride, vinyl(meth)acrylic compounds, for example vinyl(meth)acrylate, (meth)allyl(meth)acrylic compounds, for example (meth)allyl(meth)acrylate, (meth)allyl(meth)acrylate ethoxylated with 1 to 30 mol ethylene oxide per hydroxyl group, di(meth)allyl esters of polycarboxylic acids, for example di(meth)allyl maleate, di(meth)allyl fumarate, di(meth)allyl succinate or di(meth)allyl terephthalate, compounds with 3 or more ethylenically unsaturated, radically polymerisable groups such as for example glycerine tri(meth)acrylate, (meth)acrylate esters of glycerine ethoxylated with preferably 1 to 30 mol ethylene oxide per hydroxyl group, trimethylolpropanetri(meth)acrylate, tri(meth)acrylate esters of trimethylolpropane which is alkoxyated, preferably ethoxylated, preferably with 1 to 30 mol alkylene oxide per hydroxide group, trimethacrylamide, (meth)allylidenedi(meth)acrylate, 3-allyloxy-1,2-propanedioldi(meth)acrylate, tri(meth)allylcyanurate, tri(meth)allylisocyanurate, pentaerythritoltetra(meth)acrylate, pentaerythritoltri(meth)acrylate, (meth)acrylic acid esters of pentaerythritol which is ethoxylated with preferably 1 to 30 mol ethylene oxide per hydroxyl group, tris(2-hydroxyethyl)isocyanuratetri(meth)acrylate, trivinyltrimellitate, tri(meth)allylamine, di(meth)allylalkylamines, for example di(meth)allylmethylamine, tri(meth)allylphosphate, tetra(meth)allylethylenediamine, poly(meth)allyl ester, tetra(meth)allyloxyethane or tetra(meth)allylammonium halides.

As compounds of cross-linker class II are preferred compounds which have at least two functional groups which can react in a condensation reaction (=condensation cross-linkers), in an addition reaction or in a ring opening reaction with the functional groups of the monomers ( $\alpha 1$ ) or ( $\alpha 2$ ), preferably with acidic groups of the monomers ( $\alpha 1$ ). These functional groups of the compounds of cross-linker class II are preferably alcohol, amine, aldehyde, glycidic, isocyanate, carbonate or epichloro functions.



As examples of compounds of cross-linker class II are mentioned polyols, for example ethylene glycol, polyethylene glycols such as diethylene glycol, triethylene glycol and tetraethylene glycol, propylene glycol, polypropylene glycols such as dipropylene glycol, tripropylene glycol or tetrapropylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,4-pentanediol, 1,6-hexanediol, 2,5-hexanediol, glycerine, polyglycerine, trimethylolpropane, polyoxypropylene, oxyethylene-oxypropylene block copolymers, sorbitan-fatty acid esters, polyoxyethylene sorbitan-fatty acid esters, pentaerythritol, polyvinylalcohol and sorbitol, aminoalcohols, for example ethanolamine, diethanolamine, triethanolamine or propanolamine, polyamine compounds, for example ethylenediamine, diethylenetriamine, triethylenetetraamine, tetraethylenepentaamine or pentaethylenehexamine, polyglycidyl ether compounds such as ethyleneglycoldiglycidyl ether, polyethyleneglycoldiglycidyl ether, glycerinediglycidyl ether, glycerinepolyglycidyl ether, pentaerythritolpolyglycidyl ether, propyleneglycoldiglycidyl ether, polypropyleneglycoldiglycidyl ether, neopentylglycoldiglycidyl ether, hexanediolglycidyl ether, trimethylolpropanepolyglycidyl ether, sorbitolpolyglycidyl ether, phthalic acid diglycidyl ester, adipinic acid diglycidyl ether, 1,4-phenylenebis(2-oxazoline), glycidol, polyisocyanates, preferably diisocyanates such as 2,4-toluenediisocyanate and hexamethylenediisocyanate, polyaziridine compounds such as 2,2-bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate], 1,6-hexamethylenediethylene urea and diphenylmethane-bis-4,4'-N,N'-diethylene urea, halogen epoxides for example epichloro- and epibromohydrin and  $\alpha$ -methylepichlorohydrin, alkylene carbonates such as 1,3-dioxolane-2-one (ethylene carbonate), 4-methyl-1,3-dioxolane-2-one (propylene carbonate), 4,5-dimethyl-1,3-dioxolane-2-one, 4,4-dimethyl-1,3-dioxolane-2-one, 4-ethyl-1,3-dioxolane-2-one, 4-hydroxymethyl-1,1-dioxolane-2-one, 1,3-dioxane-2-one, 4-methyl-1,3-dioxane-2-one, 4,6-dimethyl-1,3-dioxane-2-one, 1,3-dioxolane-2-one, poly-1,3-dioxolane-2-on, polyquaternary amines such as condensation products from dimethylamines and epichlorohydrin. Further preferred compounds of the cross-linker class II are in addition polyoxazolines such as 1,2-ethylenebisoxazoline, cross-linkers with silane groups such as  $\gamma$ -



glycidoxypropyltrimethoxysilane and  $\gamma$ -aminopropyltrimethoxysilane, oxazolidinones such as 2-oxazolidinone, bis- and poly-2-oxazolidinone and diglycolsilicates.

- 5 Preferred compounds of class III are hydroxyl or amino group-containing esters of (meth)acrylic acid, such as for example 2-hydroxyethyl(meth)acrylate, as well as hydroxyl or amino group-containing (meth)acrylamides, or mono(meth)allylic compounds of diols.
- 10 The polyvalent metal cations of cross-linker class IV are derived preferably from singly or multiply charged cations, the singly charged in particular from alkali metals such as potassium, sodium, lithium, wherein lithium is preferred. Preferred doubly charged cations are derived from zinc, beryllium, alkaline earth metals such as magnesium, calcium, strontium, wherein magnesium is preferred. Further
- 15 cations applicable according to the invention, with higher charge, are cations from aluminium, iron, chromium, manganese, titanium, zirconium and other transition metals as well as double salts of such cations or mixtures of the named salts. The use of aluminium salts and alums and various hydrates thereof such as e.g.  $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ ,  $\text{NaAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ,  $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  or  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{-}18 \text{H}_2\text{O}$  is
- 20 preferred.

The use of  $\text{Al}_2(\text{SO}_4)_3$  and its hydrates as cross-linkers of the cross-linker class IV is particularly preferred.

- 25 Preferred water-absorbing polymers are those which are cross-linked respectively by cross-linkers of the following cross-linker classes or by cross-linkers of the following combinations of cross-linker classes: I, II, III, IV, I II, I III, I IV, I II III, I II IV, I III IV, II III IV, II IV or III IV. The above combinations of cross-linker



classes represent respectively a preferred embodiment of cross-linkers of a water-absorbing polymer particle.

Further preferred embodiments of the polymers are polymers which are cross-linked by any of the above named cross-linkers of cross-linker class I. Among these, water soluble cross-linkers are preferred. In this context, N,N'-methylenebisacrylamide, polyethylene glycol di(meth)acrylates, triallylmethylammonium chloride, tetraallylammonium chloride as well as allylnonaethylene glycol acrylate made with 9 mol ethylene oxide per mol acrylic acid are particularly preferred.

As water soluble polymers ( $\alpha 4$ ), water soluble polymers such as partially or fully saponified polyvinyl alcohol, polyvinylpyrrolidone, starches or starch derivatives, polyglycols or polyacrylic acids can be comprised in, preferably polymerised into, the water-absorbing polymer particles. The molecular weight of these polymers is not critical, as long as they are water soluble. Preferred water soluble polymers are starches or starch derivatives or polyvinyl alcohol. The water soluble polymers, preferably synthetic like polyvinyl alcohol, can also serve as graft basis for the monomers to be polymerised.

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As additives ( $\alpha 5$ ), suspension agents, odour binders, surface-active agents, or antioxidants are preferably comprised in the water-absorbing polymer particles.

The above described polymer particles comprised in the powdery water-absorbing polymers according to the invention are preferably produced by bulk polymerisation which occurs preferably in kneading reactors such as extruders or by belt polymerisation, solution polymerisation, spray polymerisation, inverse emulsion polymerisation and inverse suspension polymerisation. Solution polymerisation is preferably carried out in water as solvent. The solution polymerisation can occur



continuously or discontinuously. The solution polymerisation preferably occurs as continuously running band polymerisation. From the prior art a broad spectrum of variation possibilities can be learnt with respect to reaction proportions such as temperatures, type and quantity of the initiators as well as of the reaction solution.

5 Typical processes are described in the following patent specifications: US 4,286,082, DE 27 06 135, US 4,076,663, DE 35 03 458, DE 40 20 780, DE 42 44 548, DE 43 23 001, DE 43 33 056, DE 44 18 818. The disclosures are included here by reference and form thereby part of the disclosure.

10

In order to convert the water absorbing polymers obtained by the above-cited polymerisation processes into a particulate form with an average particle size of at least 100 µm, preferably of less than 150 µm and particularly preferably of less than 200 µm, after their separation from the reaction mixture, these polymers can  
15 first be dried at a temperature in a range of 20 to 300°C, preferably within a range of 50 to 250°C and particularly preferably within a range from 100 to 200°C to a water content of less than 40 wt. %, preferably of less than 20 wt. % and even more preferably of less than 10 wt. %, respectively based on the total weight of the polymer. The drying occurs preferably in ovens or driers known to the skilled  
20 person, for example in belt driers, drying hurdles ("Hordentrockner"), rotary kilns, fluid bed driers, disc driers, paddle driers or infrared driers. Should the thus obtained, dried polymers not yet be present in particulate form, then they must be further comminuted after the drying. The comminuting preferably occurs by dry-grinding, preferably by dry-grinding in a hammer mill, a pin mill, a ball mill or a  
25 roll mill.

Besides the above described process for transforming the polymers into a particulate form, the polymers can also be comminuted in the gel state by the process of wet grinding with any conventional device for wet grinding.

30



In another preferred embodiment, the water absorbing polymer particles comprised in the powdery water absorbing polymer are based on biodegradable materials. Natural polysaccharides belong to this group, which already naturally comprise carboxyl groups or have been provided by subsequent modification with carboxyl groups. In the first group of polysaccharides can be counted for example starches, amylose, amylopectin, celluloses and polygalactomannanes such as guar and locust bean gum, in the second group can be counted for example xanthane, alginates, gum arabic.

In a further preferred embodiment, the water absorbing polymer particles comprised in the powdery water absorbing polymers are based on a mixture of biodegradable and synthetic water absorbing polymer particles.

It is further preferred according to the invention that the water absorbing polymer particles comprise an inner portion, an outer portion surrounding the inner portion as well as a surface portion surrounding the outer portion, whereby the outer portion has a higher degree of crosslinking than the inner portion, so that preferably a core-shell structure forms. The increased crosslinking in the surface portion of the powdery water absorbing polymer is preferably achieved by means of secondary crosslinking of reactive groups near to the surface. This secondary crosslinking can occur thermally, photochemically or chemically. As secondary crosslinker for the chemical secondary crosslinking, compounds are preferred which were mentioned as crosslinker ( $\alpha 3$ ) of crosslinker classes II and IV. Particularly preferred as secondary crosslinker is ethylene carbonate.

In the process according to the invention for producing powdery water absorbing polymers, as components are preferred:

- 0.01 to 20 wt. %, preferably 0.1 to 15 wt. % and even more preferably 1 to 10 wt. % of a fine particle which is preferably not based on water absorbing crosslinked poly(meth)acrylates with an average particle size deter-



mined by sieve analysis of less than 200  $\mu\text{m}$ , preferably of less than 100  $\mu\text{m}$  and particularly preferably of less than 50  $\mu\text{m}$ ;

- 0.001 to 10 wt. %, preferably 0.01 to 5 wt. % and particularly preferably 0.5 to 1 wt. % of a thermoplastic adhesive,
- 5        - 60 to 99.998 wt. %, preferably 70 to 99 wt. % and particularly preferably 90 to 95 wt. % of a water absorbing polymer particle with an average particle size determined by sieve analysis of at least 200  $\mu\text{m}$ , preferably of at least 250  $\mu\text{m}$  and particularly preferably of at least 300  $\mu\text{m}$ , whereby the sum of the above components amounts to 100 wt. %,
- 10       - are brought together into contact at a temperature within the range of 120 to 250°C, preferably 150 to 220°C and particularly preferably 170 to 200°C.

In a design of the above process, as further component additionally at least one of  
15       the above defined secondary crosslinkers is used. In this case it is preferred that the water-absorbing fine particle is not secondary or respectively surface crosslinked. It is further preferred in this design that thermoplastic adhesive and secondary crosslinker are used in a liquid phase, preferably in an aqueous solution, whereby the concentrations given above in the context of the liquid phase are  
20       also preferred here. In this context it is preferred that as further component, a secondary crosslinker is brought into contact. It is here particularly preferred that the secondary crosslinker and the thermoplastic adhesive are added together to the other components, whereby at least the secondary crosslinker can be present in a liquid phase.

25

As water absorbing polymer particles, thermoplastic adhesives and fine particles, those water absorbing polymer particles, thermoplastic adhesives or fine particles are preferred which have already been mentioned in the context of the powdery water absorbing polymers according to the invention.

30



It is preferred according to the invention that the thermoplastic adhesives are used in particulate form, preferably in the form of a powder or of a granulate, whereby at least 50 wt. %, preferably at least 70 wt. % of the powder or of the granulate has a particle size determined by sieve analysis within a range of 1 to 200  $\mu\text{m}$ , particularly preferably within a range of 10 to 150  $\mu\text{m}$  and even more preferably within a range of 20 to 120  $\mu\text{m}$ .

Should the thermoplastic adhesives mentioned in the context of the powdery water absorbing polymers according to the invention not be present in particulate form after their production or their delivery, in particular for example if they are present in the form of blocks, these can be transformed by comminuting processes known to the skilled person, such as for example by grinding or by extruding through breaker plates and then comminuting the extruded particles into a particulate form with the necessary average particle size. Optionally, particular grinding processes can be used, for example cryogrinding at low temperatures, in particular at temperatures below the melt or glass transition temperature of the used thermoplastic adhesive. An important requirement for the grinding to the desired particle size is the brittleness of the melt adhesive.

The bringing together of water absorbing polymer particles, thermoplastic adhesives and fine particles can occur in any way. A requirement for the production of the powdery water absorbing polymers according to the invention is, however, that at least a contact time between water absorbing polymer particles, thermoplastic adhesive and fine particle is complied with, which allows an adhesive binding mediated by the thermoplastic adhesive between at least one water absorbing polymer particle and at least one fine particle. Preferably, the contact time is measured so that aggregates are generated which are as small as possible, which ideally comprise respectively only one water absorbing polymer particle and one or more fine particle applied to the surface of the water absorbing polymer particle by means of the thermoplastic adhesive. It should preferably be avoided that agglomerates consisting of several water absorbing polymer particles should form



by the adhesive effect of the thermoplastic adhesive by contact times which are too long.

5 The bringing together of the water absorbing polymer particles, the thermoplastic adhesive and the fine particles can occur in any way according to the process according to the invention. Thus, for example the thermoplastic adhesives in particulate form as well as the fine particles, can already be brought into contact with the water absorbing polymer particles during the production process for the water absorbing polymer particles. For this purpose, it is for example suitable to contact  
10 the water absorbing polymer particles with a thermoplastic adhesive particles and the fine particles during a secondary crosslinking of the water absorbing polymer particles, as is often carried out in the production of superabsorbers.

15 With respect to the order of bringing into contact the individual components, different ways of proceeding are possible.

In an embodiment of the process according to the invention, first the water absorbing polymer particles are mixed with the particulate thermoplastic adhesive in the solid state. The water absorbing polymer particles brought into contact with  
20 the thermoplastic adhesive in this way can then be mixed with the fine particles. In order to effect an adhesion, mediated by the thermoplastic adhesive, of the fine particles to the surface of the water absorbing polymer fine particles, the thermoplastic adhesive must first be heated by means of a temperature increase to a temperature above the melt or glass transition temperature, so that it has a sticky behaviour. The heating can occur to a time at which the water absorbing polymer  
25 particles have been brought into contact with the thermoplastic adhesive but not yet with the fine particles. In this case, the mixture of the polymer fine particles and the thermoplastic adhesive is correspondingly heated to a temperature above the melt temperature of the thermoplastic adhesive and this mixture is then  
30 brought into contact with the fine particles. In order to prevent an undesired agglomeration of the water absorbing polymer particles, it can be advantageous to



cool temporarily the polymer particles which have been brought into contact with the adhesive to a temperature below the melt temperature of the thermoplastic adhesive. During this cooling phase, the water absorbing polymer particles should be moved. A movement of this type can be caused for example by stirring, shaking or flowing or the like. After the bringing into contact of the water absorbing polymer particles coated with the thermoplastic adhesive with the fine particles, the temperature must be increased again to a temperature above the melt or glass transition temperature of the thermoplastic adhesive, in order to ensure an adhesion between the water absorbing polymer particles and the fine particles. In addition, in another design of the process according to the invention, the water absorbing polymer particles can be first mixed with the fine particles and then the thermoplastic adhesive can be added, followed by the warming in order to melt the thermoplastic adhesive. In this way a more homogeneous mixture of the fine particles with the water absorbing polymer particles can be achieved, which leads to less dust formation and an improved flowability.

It is however also possible to heat the thermoplastic adhesive to a time at which it has not yet been brought into contact with the water absorbing polymer particles. In this case, first the thermoplastic adhesive is heated to a temperature above the melt or glass transition temperature of the thermoplastic adhesive and then brought into contact with the water absorbing polymer particles. The water absorbing polymer particles brought into contact with the thermoplastic adhesive in this way are then mixed with the fine particles, whereby a temporary cooling to prevent formation of larger agglomerates can also occur here.

In a further embodiment of the process according to the invention, it is proceeded as above, with the difference that first the fine particles are mixed with the particulate thermoplastic adhesive in solid form and then the fine particles which have been brought into contact with the thermoplastic adhesive are mixed with the water absorbing polymer particles.



In a particularly preferred embodiment of the process according to the invention, however, the fine particles, the water absorbing polymer particles and the thermoplastic adhesive are brought together into contact at the same time. Thus, the thermoplastic adhesive in particulate form can be mixed with the water absorbing polymer particles and the fine particles at a temperature below the melt temperature and the thus-obtained mixture then heated to a temperature above the melt temperature of the thermoplastic adhesive, in order to ensure the adhesion by the thermoplastic adhesive between the fine particles and the water absorbing polymer particles. It is also possible, first to heat the thermoplastic adhesive to a temperature above the melt temperature and to mix the thus-heated thermoplastic adhesive together with the fine particles and the water absorbing polymer particles. It can also be sensible in this embodiment of the process according to the invention, to prevent an undesired agglomeration of the water absorbing polymer particles, to cool the polymer particles brought into contact with the adhesive temporarily to a temperature below the melt or glass transition temperature of the thermoplastic adhesive. During this cooling phase, the water absorbing polymer particles should be moved.

The bringing into contact of the water absorbing polymer particles with the thermoplastic adhesive and the fine particles can occur in mixing aggregates known to the skilled person. Suitable mixing aggregate components are, e.g., the Patterson-Kelley mixer, DRAIS turbulence mixer, Lödige mixer, Ruberg mixer, screw mixer, plate mixer and fluidised bed mixer as well as continuously-conveying, preferably vertical mix ovens, in which the particles are mixed with a rapid frequency by means of rotating knives and which have movable, heated conveying means.

It is preferred according to the invention if the powdery water absorbing polymers are secondary crosslinked in the surface portion in a further process step, whereby those secondary crosslinkers are preferred which have already been mentioned in



the context of the powdery water absorbing polymers according to the invention as preferred secondary crosslinkers.

5 There are various possibilities for the timing of the secondary crosslinking during the process according to the invention.

10 In one embodiment of the process according to the invention the secondary crosslinking occurs before the water absorbing polymer particles have been brought into contact with the thermoplastic adhesive and the fine particles. In this case, the polymer fine particles are brought into contact with the secondary crosslinker, preferably with a fluid comprising a solvent, preferably water, organic solvents such as methanol, ethanol, 1-propanol or 2-propanol, or a mixture of at least two thereof, and the secondary crosslinker. The water absorbing polymer particles which have been brought into contact with the secondary crosslinker are  
15 then heated to a temperature within a range of 50 to 300°C, preferably within a range of 100 to 250°C and particularly preferably within a range of 150 to 200°C, in order to carry out the secondary crosslinking. The thus secondary crosslinked polymer particles are then brought into contact as described above with the thermoplastic adhesive and the fine particles.

20

In another embodiment of the process according to the invention, the secondary crosslinking is carried out after the water absorbing polymer particles have been brought into contact with the thermoplastic adhesive and the fine particles. In this case, the powdery water absorbing polymers, in whose surface portion the fine  
25 particles are immobilized by means of the thermoplastic adhesive, are secondary crosslinked in the above-described type and way.

In a preferred embodiment of the process according to the invention, the secondary crosslinking occurs during the bringing into contact of the water absorbing  
30 polymer particles with the thermoplastic adhesive and the fine particles. It is here particularly preferred that the water absorbing polymer particles with the prefera-



bly particulate thermoplastic adhesive, the fine particles and the secondary crosslinker, preferably with the secondary crosslinker in the form of a fluid comprising the secondary crosslinker and a solvent, is mixed and then heated to a temperature above the melt temperature.

5

Preferably, the secondary crosslinker is used in a quantity within a range of 0.01 to 5 wt. %, particularly preferably within a range of 0.3 to 3 wt. % and even more preferably in a quantity within a range of 0.5 to 1.5 wt. %, respectively based on the weight of the water absorbing polymer particles. If the secondary crosslinker is used in the form of a fluid, preferably in the form of an aqueous solution or dispersion, this fluid comprises the secondary crosslinker preferably in a quantity within a range of 10 to 80 wt. %, particularly preferably in a quantity within a range of 30 to 70 wt. % and even more preferably in a quantity within a range of 40 to 50 wt. %, respectively based on the total weight of the fluid.

15

The invention also relates to the powdery water absorbing polymers obtainable by the above-described process, whereby these powdery water absorbing polymers preferably have the same properties as the powdery water absorbing polymers according to the invention as described previously.

20

Particularly preferably, the powdery water absorbing polymers obtainable by the process according to the invention are characterized by

P1 A flow value (FFC) within the range of 1 to 13, preferably within the range of 3 to 9 and particularly preferably within the range of 4 to 8 and even more preferably within the range of 5 to 7; or

P2 A dust portion of at most 6, preferably at most 4, particularly preferably at most 2.

30

It is further preferred according to the invention that the powdery water absorbing polymers according to the invention and the powdery water absorbing polymers



obtainable by the process according to the invention have at least one, preferably all of the following properties:

- 5           P3       An attrition index  $A_i$  within the range of 1 to 17, preferably within the range of 1.1 to 15 and particularly preferably within the range of 1.5 to 10;
- P4:     An attrition difference  $A_d$  within the range of 0 to 7, preferably within the range of 1.1 to 6 and particularly preferably within the range of 1.5 to 3;
- 10          P5:     A retention determined according to ERT 441.1-99 of at least 20 g/g, preferably at least 25 g/g and particularly preferably at least 27 g/g as well as even more preferably within the range of 27 to 35 g/g.

15           The property combinations arising from the above properties P1 to P5 of two or more of these properties respectively represent preferred embodiments of the present invention. Further preferably, the powdery water absorbing polymers according to the invention have the following properties or property combinations represented as follows by letters or combinations of letters: P1P3P4P5, P1P5, P1P3P5, P3P5 or P1P2P3P4P5.

20           In one embodiment, the invention relates to a powdery water absorbing polymer comprising two at least 30 wt. %, preferably at least 75 wt. % and particularly preferably at least 95 wt. % a crosslinked, partially neutralized, preferably neutralized within the range of 60 to 80 mol. %, polyacrylic acid and with at least one, preferably all of the properties P1 to P5, preferably the property combinations

25           P1P3P4P5, P1P5, P1P3P5 and even more preferably the property combination P3P5.

          It is further preferred that at least 50 wt. %, particularly preferably at least 70 wt. % and even more preferably at least 90 wt. % of the powdery water absorbing

30           polymers obtainable by the process according to the invention as well as the powdery water absorbing polymers according to the invention have a particle size de-



terminated by sieve analysis within the range of greater than 50 to 2,000  $\mu\text{m}$ , preferably in a range of 100 to 1,500  $\mu\text{m}$  and even more preferably in a range of 200 to 1,200  $\mu\text{m}$ .

5 In the transport process according to the invention, the powdery water absorbing polymers obtainable by the process according to the invention or the powdery water absorbing polymers according to the invention flow through a pipe, whereby the pipe preferably forms a part of an installation for producing a water absorbing polymer or of a dosing system for a water absorbing polymer. Dosing  
10 systems of this type can, for example, be used in charging containers or bags or are situated in Airlaid or diaper machines. Particularly preferably, the pipe is the pipe in which the powdery water absorbing polymers are conducted when they are brought into contact with a fibrous material, such as for example cotton fibres, to form respectively an absorbent core or nucleus ("Kern").

15 The composite according to the invention comprises an above-defined powdery water absorbing polymer and a substrate. Preferably, the powdery water absorbing polymer according to the invention and the substrate are fixed together. As substrates, layers made from polymers, such as for example from polyethylene, polypropylene or polyamide, metals, non-woven materials, fluff, tissues, webs, natural  
20 or synthetic fibres or other foams, are preferred.

As composite, according to the invention are preferred sealant materials, cables, absorbent cores as well as diapers and hygiene articles comprising these.

25 In the process according to the invention for producing a composite, a powdery water absorbing polymer according to the invention or a powdery water absorbent polymer obtainable by the process according to the invention and a substrate and optionally a suitable auxiliary are brought into contact with each other. The bringing  
30 into contact preferably occurs by Wetlaid and Airlaid processes, compacting, extruding and mixing.



The invention additionally relates to a composite which is obtainable by the above process.

5 The invention further relates to chemical products, in particular foams, formed bodies, fibres, sheets, films, cables, sealant materials, liquid-absorbing hygiene articles, carriers for plant or fungus growth regulating agents or plant protection active substances, additives for building materials, packaging materials or soil additives, which comprise the powdery water absorbing polymer according to the  
10 invention or the powdery water absorbing polymer obtainable by the process according to the invention or the above-described composite. The chemical products are characterized in particular by a particularly good biodegradability.

In addition, the invention relates to the use of the powdery water absorbing polymer according to the invention or the powdery water absorbing polymer obtain-  
15 able by the process according to the invention or of the above-described composite in hygiene products, in fighting floods, in insulation against water, in regulation of the water management in soil or in treating food products.

20 Finally, the invention also relates to the use of a thermoplastic adhesive for alteration of the flow value (FFC) or of the dust portion in powdery water absorbing polymers comprising this thermoplastic adhesive with respect to powdery water absorbing polymers which do not comprise this thermoplastic adhesive, whereby as thermoplastic adhesive, those adhesives are preferred which have already been  
25 mentioned in the context of the powdery water absorbing adhesives according to the invention.

The invention is now more closely described by means of test methods and non-limiting examples.

30



## TEST METHODS

### DETERMINATION OF THE FFC VALUE

- 5 The FFC value gives information regarding the flow properties of a bulk material in a silo. In the measurement, the bulk material is subjected to different stresses. The flow behaviour can be characterized as follows;

	FFC < 1	non-flowing
10	1 < FFC < 2	very cohesive
	2 < FFC < 4	cohesive
	4 < FFC < 10	slightly flowing
	10 < FFC	free flowing

- 15 A good flow behaviour is present if a bulk material can be made to flow without great effort, e.g. if the bulk material runs out of a funnel or of a silo without consolidation. With poorly flowing bulk materials, disruptions of the running out occur or they consolidate during transport or storage. With the term “to flow” is meant that the bulk material deforms in a plastic manner because of stress.

20

- Further details regarding the exact conducting of the test for determination of FFC can be found in the articles from Dr. Ing. Ditmar Schulze “Das automatische Ringschwergerät RST-01.pc” from February 2002 and “Fliesseigenschaften von Schüttgütern und verfahrenstechnische Siloauslegung” from the year 2002. In the present measurements, the manually operated variant of the circular shear apparatus RST-01.01 is used.

### DETERMINATION OF THE DUST PORTION

- 30 The dust portion is determined with an apparatus of the company Palas, Germany of the type “Dust View”. To this end, a sample of 30.00 g is placed in a funnel



pipe. At the start of the measurement, the funnel flap opens automatically and the sample falls into a dust reservoir. The reduction of a laser beam (reduction of the transmission) is measured by the dust formation. This value serves for the determination of the dust portion, i.e. the cloudiness, in percent with a scale from 1 to 100. The dust portion is given by a start value at the start of the measurement and a dust value measured after 30 seconds for determining the floating portion. Thus the dust portion is given by the sum of the start value and the dust value.

#### DETERMINATION OF THE ATTRITION INDEX AND THE ATTRITION DIFFERENCE

10

The test device represented in Figure 1 is used for this purpose. This consists of a funnel 1 for introducing a sample into a probe chamber 2. Between the funnel and the probe absorption chamber 2, a conduit is provided, with a charging valve V1 and a feed line provided with a gas regulating valve V2 arranged under charging valve V1. By means of V2, a pressure of 4.3 bar is applied to the sample absorption chamber 2. This consists of a cylinder with a diameter of 9 cm and a length of 16 cm. A blunt cone-shaped lower region is attached to this cylinder, said lower region having a lower opening with a diameter of 4 cm. To this is attached a 2 cm long pipe with a diameter of 4 cm, which leads intern to a further blunt cone-shaped cycle with a length of 4.5 cm and a lower diameter of 1.75 cm. To this is attached a chamber outlet valve V3. From V3, a pipe-conduit with an inner diameter of 10 mm and a total length of 1101 cm follows via a curved piece of 90 degrees and of 4.5 cm length. The pipe conduit begins with a straight section of 30 cm, followed by 16 straight sections each with a length of 60 cm linked with curved piece of 90 degrees and of 4.5 cm length, the 16 straight sections being joined together via 180 degrees curved sections of respectively 4.5 cm. To the 16 sections is attached a further straight section of 30 cm length via a curved piece of 90 degrees and 4.5 cm length. This section leads into a sample collection chamber 4, which only differs in its construction from chamber 2 in that instead of the upper cover, a filter bag with a substantially smaller pore size in comparison to the particle size of the samples is applied. The sample collection chamber is sealed

30



below by a sample removal valve V4. All metal parts of the above-described test device are made from 316 alloy stainless steel. The tubes are standard stock pipes. The inner surfaces of the individual components of the device are smooth. Valves of the type 20 SS0R-02-LL-9102 from the company Milwaukee Valve Company, USA were used.

The above described device is operated as follows:

#### Step 1 - Sample Charging

The valves V1, V4 are open, valves V2 and V3 are closed. 50 g of a sample is loaded into chamber 2 using funnel 1.

#### Step 2 - Sample transport

The valves are activated in the following order: a) V1 closed, b) V2 opened, c) V3 closed. After the pipe shows no more oscillation caused by passage of the sample, the following valve positions are set: a) V2 closed, V1 open, V3 closed.

#### Step 3 - Sample removal

To remove the sample, a vessel is placed under V4 and by carefully opening V4 the sample is loaded into the vessel for further investigation. V4 is then closed again.

The sample is subjected to the determination according to DIN 55992-2 both before step 1 and after step 3 for the determination of the dust portion before ( $S_{vorA}$ ) and after attrition ( $S_{nachA}$ ).

The "attrition index "A" is given by  $A_j = S_{afterA}/S_{beforeA}$ .



The “attrition difference”  $A_d$  is given by  $A_d = S_{\text{after}\Delta} - S_{\text{before}\Delta}$ .

#### EXAMPLES

- 5 In the following examples a particulate, lightly crosslinked, partially neutralized polyacrylic acid is used as pre-product, which is commercially obtainable from the company Stockhausen GmbH & Co. KG under the trade name FAVOR<sup>®</sup> of the type Z3050. This has a retention of 33 g/g and a dust portion of 3.7.

10 EXAMPLE 1

Production of the powdery water absorbing polymer according to the invention:

- 15 1000 g of the pre-product were placed with the quantities given in table 1 of fine particles and thermoplastic adhesive in a vertical mixer (MTI-Mischtechnik Industrieanlagen GmbH, type LM 1.5/5) and combined at 750 rpm with 40 g 25 wt. % ethylene carbonate solution.

- 20 The coated pre-product was transferred to a Gericke powder conveyor (Gericke GmbH, type GLD 75) and conveyed continuously with a conveyor performance of 20 g/min into a Labor-Nara-reactor (HTM Reetz GmbH, type Laboratory paddle mixer “Mini-Nara II”). The dwell time in the dryer was approx. 90 minutes and the product was heated to a maximum temperature of 185 to 195°C. During this time, the secondary crosslinking occurred and the thermoplastic adhesive was  
25 melted, influenced the flow behaviour, distributed itself on the surface and bound the fine particles to the surface of the water absorbing polymer particles.

Table 1

Experiment	Fine parti-	Quantity	Thermoplastic	Quantity of	FFC	Dust
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number	cles	of fine particles	adhesive	thermoplastic adhesive		portion
1 (HBr 7/127)	Mg HPO <sub>4</sub> · 3 H <sub>2</sub> O (< 50 µm)	1.0 wt. %	SchaettiFix <sup>®</sup> 386 <sup>1)</sup>	0.5 wt. %	5.4	0.2
2 (HBr 7/128)	Technocell <sup>®</sup> 75 (cellulose fibre < 75 µm)	1.0 wt. %	SchaettiFix <sup>®</sup> 386 <sup>1)</sup>	0.5 wt. %	4.3	0.1

<sup>1)</sup> Product of the company Schaetti AG, Zurich, Switzerland; melting range: 130 to 160°C, melt viscosity at 160°C: 520 Pas, thermal stability: 120°C.

#### EXAMPLE 2

5

The results collected in table 2 were produced as described in example 1 with the materials and quantities given in table 2 and 60 g of the 25 wt. % ethylene carbonate solution. The samples were subjected to the attrition test. The FFC value was determined after carrying out the attrition test. The CRC value was determined before and after carrying out the attrition test.

10

Table 2

	Control	Vestamelt <sup>®2)</sup> 4481	SchaettiFix <sup>®</sup> 386
Experiment number	3	4	5
Quantity of thermoplastic adhesive	-	0.3 wt. %	0.3 wt. %
Dust portion <sup>3)</sup> S <sub>beforeA</sub>	0.44	0.40	0.39
Dust portion <sup>3)</sup> S <sub>afterA</sub>	7.53	3.48	3.05
A <sub>i</sub>	17.11	8.7	8.97



A <sub>d</sub>	7.09	3.08	2.66
FFC before attrition test	8.7	4.6	5.0
CRC value before attrition test [g/g]	27.3	27.5	27.2

<sup>2)</sup> product of Degussa AG, Düsseldorf, Germany

<sup>3)</sup> quadruple determination

### EXAMPLE 3

5

Production of a powdery water absorbing polymer by coating with a thermoplastic adhesive in the presence of superabsorber fine particles;

1000 g of the pre-product was placed with the quantities given in table 3 of thermoplastic adhesive in a vertical mixer (MTI-Mischtechnik Industrieanlagen GmbH; type LM 1.5/5) and coated at 750 rpm with 40 g 25 wt. % ethylene carbonate solution.

The coated pre-product was transferred into a Gericke powder conveyor (Gericke GmbH, type GLD 75) and conveyed continuously with a conveyor performance of 20 g/min into a Labor-Nara reactor (HTM Reetz GmbH, type laboratory paddle mixer "Mini-Nara II"). The dwell time in the dryer was approximately 90 minutes and the product was heated to a maximum temperature of 185 to 195°C. During this time, the secondary crosslinking occurred and the thermoplastic adhesive was melted, influenced the flow behavior and distributed itself on the surface.

Table 3

Experiment number	Fine particles	Quantity of fine	Thermoplastic adhesive	Quantity of thermoplastic	FFC	Dust portion
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		particles		adhesive		
6 (HBr 7/126)	-	-	SchaettiFix <sup>®</sup> 386	0.5 wt. %	5.1	0.4
7 control (HBr 7/125)	-	-	-	-	-	4.5

The examples show that by the use of thermoplastic adhesives, both the superabsorber fine particles which accompany the water absorbing polymer and also further fine particles which are different to the water absorbing polymer can be bound to water absorbing polymer particles with high stability and reduction of the dust portion, without the absorption properties such as retention of the thus-obtained water absorbing polymer particles, or flowability, suffering.



## CLAIMS

1. Powdery water-absorbing polymers comprising as components:
  - 5       - 0.01 to 20 wt.% of a fine particle with a particle size of less than 200  $\mu\text{m}$ ,
  - 0.001 to 10 wt.% of a thermoplastic adhesive,
  - 60 to 99.998 wt.% of a water-absorbing polymer particle with a particle size of 200  $\mu\text{m}$  and above,

10       wherein

      the fine particles are bound to the surface of the water-absorbing polymer particles by the thermoplastic melt adhesive and the powdery water-absorbing polymers have either

  - 15       - a flow value (FFC) within the range from 1 to 13, or
  - a dust portion of at most 6.
2. Powdery water-absorbing polymers according to claim 1, with a flow value (FFC) in the range from 1 to 13 and a dust portion of at most 6, respectively based on the total weight of the powdery water-absorbing  
20       polymers.
3. Powdery water-absorbing polymers according to claim 1 or 2, wherein the thermoplastic adhesive has a melt temperature according to ISO 11357 of at least 50 °C, preferably of at least 60 °C and even more  
25       preferably of at least 70 °C.



- 5
4. Powdery water-absorbing polymers according to any one of the preceding claims, wherein the thermoplastic adhesive has a melt viscosity according to Brookfield (ASTM E 28) with a number 27 spindle at a temperature of 160 °C of less than 2000 Pas.
- 10
5. Powdery water-absorbing polymers according to any one of the preceding claims, wherein the thermoplastic adhesive comprises a polycondensate to at least 10 wt.%, preferably at least 50 wt.% and particularly preferably at least 90 wt.%.
6. Powdery water-absorbing polymers according to claim 5, wherein the polycondensate is a polyester.
- 15
7. Powdery water-absorbing polymers according to any one of the preceding claims, wherein the fine particle comprises an organic fine particle to at least 80 wt.%, based on the weight of the fine particle.
- 20
8. Powdery water-absorbing polymers according to any one of the preceding claims, wherein the fine particle comprises an inorganic fine particle to at least 80 wt.%, based on the weight of the fine particle.
- 25
9. Powdery water-absorbing polymers according to any one of the preceding claims, wherein these are secondary crosslinked in the surface region by means of a surface crosslinker.
10. Powdery water-absorbing polymers according to claim 9, wherein the surface crosslinker comprises at least one organic compound or at least one polyvalent metal cation.



11. Powdery water-absorbing polymer comprising to at least 30 wt.% a crosslinked, partially neutralised, preferably neutralised in the range of 60 to 80 mol%, polyacrylic acid and with at least one of the following properties
- 5 P1 a flow value (FFC) within the range of 1 to 13; or
- P2 a dust portion of at most 6,
- P3 an attrition index  $A_i$  within the range of 1 to 17;
- P4 an attrition difference  $A_d$  within the range of 0 to 7,
- 10 P5 a retention determined according to ERT 441.1-99 of at least 20 g/g.
12. Process for producing powdery water-absorbing polymers, wherein as components:
- 15 - 0.01 to 20 wt.% of a fine particle with a particle size of less than 200  $\mu\text{m}$ ,
- 0.001 to 10 wt.% of a thermoplastic adhesive,
- 60 to 99.998 wt.% of a water-absorbing polymer particle with a particle size of 200  $\mu\text{m}$  and above,
- 20 are brought into contact with each other at a temperature within the range of 120 to 250 °C, preferably 150 to 220 °C and particularly preferably 170 to 200 °C.
13. Process according to claim 12, wherein the bringing into contact occurs in a continuously conveying mixing oven.
- 25 14. Process according to claim 13, wherein the oven has movable, heated conveying means.



15. Process according to any one of claims 12 to 14, wherein as further component a secondary crosslinker is brought into contact.
- 5 16. Process according to claim 15, wherein the secondary crosslinker and the thermoplastic adhesive are conducted together to the other components.
- 10 17. Process according to claim 15 or 16, wherein at least the secondary crosslinker is present in a liquid phase.
18. Powdery water-absorbing polymers, obtainable by a process according to any one of claims 12 to 17.
- 15 19. Powdery water-absorbing polymers according to claim 18 with at least one of the properties P1 to P5 defined in claim 11.
- 20 20. Powdery water-absorbing polymers according to any one of claims 1 to 11, 18 or 19, wherein at least 50 wt.% of the powdery water-absorbing polymers have a particle size within the range of greater than 50 to 2,000  $\mu\text{m}$ .
- 25 21. Transport process, wherein powdery water-absorbing polymers according to any one of claims 1 to 12, 18 or 19 flow through a channel.
22. Process according to claim 21, wherein the channel forms part of an installation for producing a water-absorbing polymer or of a dosing system for a water-absorbing polymer.



23. Composite, comprising powdery water-absorbing polymers according to any one of claims 1 to 12, 18 or 19.
- 5 24. Chemical products, comprising powdery water-absorbing polymers according to any one of claims 1 to 12, 18 or 19.
25. Use of a thermoplastic adhesive for alteration of the flow value (FFC) or the dust portion in powdery water-absorbing polymers comprising this thermoplastic adhesive with respect to powdery water-absorbing polymers not comprising this thermoplastic adhesive.
- 10



## SUMMARY

The present invention relates to powdery water-absorbing polymers, comprising as components:

- 5        -        0.01 to 20 wt.% of a fine particle with a particle size of less than 200  $\mu\text{m}$ ,
- 0.001 to 10 wt.% of a thermoplastic adhesive,
- 60 to 99.998 wt.% of a water-absorbing polymer particle with a particle size of 200  $\mu\text{m}$  and above,

10       wherein

the fine particles are bound to the surface of the water-absorbing polymer particles by the thermoplastic melt adhesive and the powdery water-absorbing polymers have either

- a flow value (FFC) within the range from 1 to 13, or
  - 15       -        a dust portion of at most 6,
- as well as a process for producing powdery water-absorbing polymers, the powdery water-absorbing polymers obtainable by this process, a transport process, a composite, chemical products as well as the use of a thermoplastic adhesive.

20

Fig. 1